



**PATENT APPLICATION FOR**

**54) POSITIVE ELECTRODE ACTIVE MATERIAL FOR NONAQUEOUS  
ELECTROLYTE BATTERY AND NONAQUEOUS ELECTROLYTE  
BATTERY**

(11)Publication number : **2001-076727**

(43)Date of publication of application : **23.03.2001**

(51)Int.Cl.

**H01M 4/58**

**H01M 4/02**

**H01M 10/40**

(21)Applicati **11-254589**  
on number :

(71)Applicant **SONY CORP**

(22)Date of **08.09.1999**  
filing :

(72)Inventor : **KUYAMA JUNJI**  
**NAGAMINE MASAYUKI**

**\* NOTICES \***

**Japan Patent Office is not responsible for any  
damages caused by the use of this translation.**

**1. This document has been translated by computer. So the translation may not reflect  
the original precisely.**

**2. \*\*\*\* shows the word which can not be translated.**

**3. In the drawings, any words are not translated.**

**RECEIVED**  
**MAY 31 2002**  
**TC 1700**

# **POSITIVE ELECTRODE ACTIVE MATERIAL FOR NONAQUEOUS ELECTROLYTE BATTERY AND NONAQUEOUS ELECTROLYTE BATTERY**

## **Technical Field of the Invention:**

[The technical field to which invention belongs] this invention relates to enhancement of the spinel type lithium compound manganic acid ghost which is an active material especially about the positive electrode for nonaqueous electrolyte cells, and a nonaqueous electrolyte cell.

## **Background of the Invention:**

[Prior art] In recent years, in connection with highly-efficient-izing of electronic equipment, a miniaturization, and portable-izing, the rechargeable battery with an energy density high as power for a drive of these electronic equipment is demanded. Although a nickel cadmium rechargeable battery, a lead accumulator, a nickel hydrogen rechargeable battery, a lithium ion rechargeable battery, etc. are mentioned as a rechargeable battery used for these electronic equipment, a cell voltage has a high-energy density highly, and especially a lithium ion rechargeable battery also has little self-discharge, and has the characteristic features, like there is no memory effect.

[0003] Now, it is common that the carbon of the layer structure is used to the cobalt acid lithium ( $\text{Li}_x\text{CoO}_2$ ,  $0 \leq x \leq 1$ ) which has the layer structure in a positive electrode at a lithium ion rechargeable battery, and the negative electrode. Although a cobalt acid lithium is the material which can show the high voltage characteristic beyond 4V, and can maintain comparatively stable structure to the dope of a lithium ion, and a \*\* dope, in cobalt's receiving the constraint like resources, since it is expensive, the utilization of a positive-electrode material which does not use cobalt is desired.

[0004] As a candidate of the positive-electrode material which does not contain cobalt, the manganic acid lithium ( $\text{LiMn}_2\text{O}_4$ ) which takes the nickel acid lithium ( $\text{Li}_x\text{NiO}_2$ ,  $0 \leq x \leq 1$ ) and Spinel structure of the layer structure is mentioned. Since it is cheap and safety is also high, especially the manganic acid lithium attracts attention as a positive-electrode material of the next generation.

[0005]

### **Summary of the Invention:**

[Effect of the invention] According to this invention, by specifying primary particle diameter and specific surface area of a spinel type lithium compound manganic acid ghost, there are few cell degradations by the manganese elution, and they can offer the positive active material for nonaqueous electrolyte cells which was excellent in the high-rate-discharge property, and a nonaqueous electrolyte cell so that clearly from the above explanation.

[Object of the Invention] However, the cell property degradation by the manganese elution to the inside of the electrolytic solution is pointed out at the time of an elevated-temperature store and a cycle, and in order to be utilization, the cell property improvement by manganese elution suppression is required for the manganic acid lithium.

### **Brief Description of the Drawings:**

[An easy explanation of a drawing]

[ Drawing 1 ] It is the outline cross section showing the example of 1 configuration of a cylindrical nonaqueous electrolyte cell.

[An explanation of a sign]

2 Positive Electrode, 3 Negative Electrode, 4 Separator, 5 Cell Can

### **Detailed Description of the Invention:**

[Detailed description]

[0001]

[The technical field to which invention belongs] this invention relates to enhancement of the spinel type lithium compound manganic acid ghost which is an active material especially about

the positive electrode for nonaqueous electrolyte cells, and a nonaqueous electrolyte cell.  
[0002]

[0006] Although to make the touch area with the electrolytic solution small by making small specific surface area of a positive active material is confirmed as indicated by for example, the publication-number 147859 [ nine to ] official report in order to prevent the elution to the inside of the electrolytic solution of manganese generally Although a manganese elution will be reduced if specific surface area is made small, making specific surface area small by one side has the problem that lead to a particle diameter becoming large, the reactivity at the time of a lithium dope \*\* dope becomes bad, and the charge-and-discharge property in a heavy load becomes bad. In order to do this reactant mischief because a diffusion of a lithium ion becomes slow when particle size becomes large and to carry out a diffusion of a lithium early, it needs for the diameter of crystal grain to be small. Thus, it is difficult to reconcile a cycle property and a heavy-load property only by controlling particle size.

[0007] this invention is proposed in order to cancel such un-arranging, and it aims at offering the manufacture technique and a nonaqueous electrolyte cell further for the purpose of offering the positive active material for nonaqueous electrolyte cells which may reconcile a cycle property and a heavy-load property.

[0008]

[The means for solving a technical problem] In order to solve the above-mentioned problem, as a result of investigating the problem of the cell degradation by the physical-properties property and manganese elution of a positive-electrode material, the manganese elution volume found out that the manganese elution volume of specific surface area for which it asked by the BET adsorption method decreased as the parvus depending on the value of the specific surface area for which it asked by the BET adsorption method. Even if primary particle diameter was small, when the primary grain formed the floc, the specific surface area for which it furthermore asked by the BET adsorption method found out becoming small, optimized baking conditions and trituration conditions, and completed this invention by controlling the value of the specific surface area for which it asked by the size and BET adsorption method of primary grain. The flocculation said here means the status that unit grain (primary grain) gathers partly with chemical bonding strength, and forms the composite particle (secondary grain).

[0009] That is, the positive active material for nonaqueous electrolyte cells of this invention comes to contain the lithium compound manganic acid ghost with a Spinel structure, and the sizes of the primary particle diameter are 0.05 micrometers or more and 10 micrometers or less, it forms the floc, and specific surface area measured by the BET adsorption method is characterized by being a domain below  $2\text{m}^2/\text{g}$  more than  $0.2\text{m}^2/\text{g}$ .

[0010] Moreover, it is characterized by using for the nonaqueous electrolyte cell of this invention the lithium compound manganic acid ghost whose specific surface area which it has a Spinel structure, and the sizes of primary particle diameter are 0.05 micrometers or more and 10 micrometers or less, form the floc, and is measured by the BET adsorption method is a domain below  $2\text{m}^2/\text{g}$  more than  $0.2\text{m}^2/\text{g}$  as a positive active material.

[0011]

[Gestalt of implementation of invention] Hereafter, the positive active material for nonaqueous electrolyte cells which applied this invention, its manufacture technique, and the nonaqueous electrolyte cell using this are explained.

[0012] In this invention, although the lithium compound manganic acid ghost which has a Spinel structure as a positive active material was used, the size of the primary particle diameter was specified as 0.05 micrometers or more and 10 micrometers or less. If primary particle diameter

becomes larger than 10 micrometers, and a high-rate-discharge property will get worse and it will become smaller than 0.05 micrometers, sufficient manganese elution depressor effect by flocculation will not be obtained.

[0013] The sizes of desirable primary particle diameter are 0.1 micrometers or more and 5 micrometers or less, and are 0.5 micrometers or more and 3 micrometers or less still preferably.

[0014] Furthermore, the value of the specific surface area measured by the BET adsorption method when the material which has the above-mentioned primary particle diameter condenses specified that it was below  $2\text{m}^2/\text{g}$  more than  $0.2\text{m}^2/\text{g}$ . Thus, it is because flocculation will also stop suppressing a manganese elution if a high-rate-discharge property will get worse if specific surface area becomes smaller than  $0.2\text{m}^2/\text{g}$ , and \*\*\*\*\* becomes large from  $2\text{m}^2/\text{g}$  as specified ground.

[0015] Among the convention domains of specific surface area, more than  $0.2\text{m}^2/\text{g}$ , a desirable domain is below  $1\text{m}^2/\text{g}$ , and is below  $0.6\text{m}^2/\text{g}$  more than  $0.25\text{m}^2/\text{g}$  still preferably.

[0016] The lithium compound manganic acid ghost (spinel type manganic acid lithium) with the above-mentioned Spinel structure can contain any one or more kinds of alloying elements of the group which consists of Ti, V, Cr, Fe, Co, nickel, and aluminum to 0.3 or less by the atomic ratio. It is because it will become difficult to maintain a Spinel structure and a cell property will fall remarkably as ground for having specified the content of an alloying element or less as 0.3 by the atomic ratio, if the content of an alloying element increases more than 0.3.

[0017] Therefore, the above-mentioned lithium compound manganese active material can be expressed with general formula  $\text{Li}_x\text{Mn}_2\text{-yMyO}_4$  (however, it is  $0.90 \leq x \leq 1.4$  and  $y \leq 0.30$ , and M expresses any one or more kinds of the group which consist of Ti, V, Cr, Fe, Co, nickel, and aluminum.).

[0018] The content of a desirable alloying element is 0.15 or less, and is 0.10 or less more preferably.

[0019] What is necessary is to mix the start raw material of a lithium compound manganic acid ghost by predetermined composition, and just to calcinate at the temperature of 600 degrees C or more and 900 degrees C or less, after carrying out pressurization molding, in order to obtain such a lithium compound manganic acid ghost.

[0020] It is because sufficient flocculation of primary grain will not happen, specific surface area will not become small, if burning temperature is lower than 600 degrees C, and big and rough-ization of primary grain will advance and primary particle diameter will become large from default value, if higher than 900 degrees C, although this invention prescribed burning temperature to 600 degrees C or more and 900 degrees C or less. Desirable burning temperature is 600 degrees C or more and 850 degrees C or less, and is 650 degrees C or more and 850 degrees C or less still preferably.

[0021] When applying to a nonaqueous electrolyte cell (for example, nonaqueous electrolyte rechargeable battery), using as a positive active material the manganic acid lithium generated as mentioned above, it can apply, for example in the combination of the following negative electrodes and electrolytic solutions.

[0022] To the negative electrode, polymers, such as a poly-acene besides carbonaceous materials, such as pyrolytic carbons, corks (pitch coke, a needle coke, petroleum coke, etc.), graphite, glassy carbons, the organic high-molecular-compound baking field (what calcinated and carried out the carbonization of phenol resin, the furan resin, etc. at suitable temperature), a carbon fiber, and active carbon, or a metal lithium, and a lithium alloy, and polypyrrole, are usable just possible [ in reversible / a dope \*\* dope ] in a lithium.

[0023] The electrolytic solution which melted this in the organic solvent is used for the electrolytic solution, using lithium salt as an electrolyte. Although not limited especially as an

organic solvent here, independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, gamma-butyrolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, a sulfo run, an acetonitrile, diethyl carbonate, and dipropyl carbonate, are usable, for example.

[0024] To the electrolyte,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiB}(\text{C}_6\text{H}_5)_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{CH}_3\text{SO}_3\text{Li}$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ , etc. are usable.

[0025] Moreover, it is applicable also about the cell using the solid electrolyte which comes to distribute an electrolyte, and the cell using the solid electrolyte of the shape of gel containing a swelling solvent not only the nonaqueous electrolyte cell using the nonaqueous electrolyte which comes to melt an electrolyte in a non-aqueous solvent but into a matrix macromolecule.

Furthermore, it is applicable not only about a rechargeable battery but a primary cell.

[0026] The cell of this invention is not limited especially about the configuration, and can make cylindrical, a square shape, a coin type, a button type, etc. a thin shape and the various sizes of a large-sized grade.

[0027] Next, the example of concrete structure and its manufacture technique of the nonaqueous electrolyte cell which applied this invention are explained.

[0028] It is the example of a cylindrical nonaqueous electrolyte cell which is shown in drawing 1. Such a nonaqueous electrolyte cell 1 is manufactured as follows.

[0029] the positive electrode where a positive electrode 2 contains a positive active material (spinel type lithium compound manganic acid ghost) and a binding agent -- a mixture is produced by [ used as collection \*\*\*\* of positive electrodes ] applying and drying uniformly and forming a positive-active-material layer, for example on metallic foils, such as an aluminum foil the above-mentioned positive electrode -- and also it can use a well-known binding agent as a binding agent of a mixture -- the above-mentioned positive electrode -- a well-known additive etc. can be added to a mixture

[0030] the negative electrode containing the carbon material from which a negative electrode 3 serves as a negative-electrode active material, and a binding agent -- a mixture is produced by [ used as collection \*\*\*\* of negative electrodes ] applying and drying uniformly and forming a negative-electrode active material layer, for example on metallic foils, such as copper foil the above-mentioned negative electrode -- and also it can use a well-known binding agent as a binding agent of a mixture -- the above-mentioned negative electrode -- a well-known additive etc. can be added to a mixture

[0031] The positive electrode 2 obtained as mentioned above and the negative electrode 3 are stuck through the separator 4 which consists of a microporosity polypropylene film, and \*\*\*\*\* is constituted by \*\*\*\*ing to a swirl type many times.

[0032] Next, an electric insulating plate 6 is inserted in the pars basilaris ossis occipitalis of the iron cell can 5 which performed nickel plating to the inside, and \*\*\*\*\* is contained further.

And in order to take \*\*\*\* of a negative electrode, the end of the negative-electrode lead 7 which consists of nickel is made to stick to a negative electrode 3 by pressure, and the other end is welded to the cell can 5. Thereby, the cell can 5 will have a negative electrode 3 and a conduction, and serves as the external negative electrode of the nonaqueous electrolyte cell 1.

Moreover, in order to take \*\*\*\* of a positive electrode 2, the end of the positive-electrode lead 8 which consists of aluminum is attached in a positive electrode 2, and the other end is electrically connected with the cell lid 10 through the sheet metal for a current cutoff 9. This sheet metal for a current cutoff 9 intercepts a current according to cell internal pressure. Thereby, the cell lid 10 will have a positive electrode 2 and a conduction, and serves as the external positive electrode of the nonaqueous electrolyte cell 1.

[0033] Next, nonaqueous electrolyte is poured in into this cell can 5. This nonaqueous electrolyte

melts an electrolyte in a non-aqueous solvent, and is prepared.

[0034] Next, by closing the cell can 5 through the insulating obturation gasket 11 which applied asphalt, the cell lid 10 is fixed and the cylindrical nonaqueous electrolyte cell 1 is produced.

[0035] In addition, in this nonaqueous electrolyte cell 1, as shown in drawing 1, while the center pin 12 linked to the negative-electrode lead 7 and the positive-electrode lead 8 was formed, when the pressure inside a cell becomes higher than a predetermined value, the PTC element 14 for preventing the safe valve gear 13 for extracting an internal gas and the temperature rise inside a cell is formed.

[0036]

[Example] Hereafter, the concrete example which applied this invention is explained based on an experimental result.

[0037] By predetermined composition, the experiment 1Li raw material, Mn raw material, and the alloying-element raw material were \*\*\*\*ed so that it might become a total of 2kg, and it mixed with the rotating type ball mill for 5 hours. It is the mixed raw material by the pressurization tablet molding machine 400kgf/cm<sup>2</sup> It cast by the pressure and baking was performed at 800 degrees C in the atmospheric-air ambient atmosphere after that for 15 hours. The calcinated active material performed trituration for 10 minutes with the oscillatory-type ball mill.

[0038] \*\*s which performs baking of 800 degrees C and 15 hours with a rotating type ball mill, without performing pressurization molding after 5 hour mixture, and strikes trituration with an oscillatory-type ball mill for 5 minutes after that as an example of a comparison, and the thing which performed trituration for 10 minutes were used

[0039] The obtained positive active material performed organization observation by SEM, and specific-surface-area measurement by the BET adsorption method, and calculated the value of primary particle diameter and specific surface area.

[0040] Thus, primary particle diameter of the obtained active material and the size of specific surface area are shown in Table 1.

[0041]

[Table 1]

	組成	1次粒子径(μm)	比表面積(m <sup>2</sup> /g)
実施例1-1	Li1.01Mn2O4	2.5	0.80
実施例1-2	Li1.02Mn1.98Co0.02O4	1.6	0.52
実施例1-3	Li0.96Mn1.90V0.10O4	4.0	1.36
実施例1-4	Li1.0Mn1.8Ni0.2O4	3.1	1.45
実施例1-5	Li1.00Mn1.85Fe0.15O4	8.2	1.95
実施例1-6	Li1.10Mn1.75Cr0.25O4	3.6	0.84
比較例1-1	Li1.03Mn0.96Ni0.04O4	0.8	2.24
比較例1-2	Li0.99Mn0.70Al0.30O4	2.3	3.58
比較例1-3	Li1.08Mn1.85Co0.15O4	5.5	0.17

[Table 1]

	組成	1次粒子径( $\mu\text{m}$ )	比表面積( $\text{m}^2/\text{g}$ )
実施例1-1	$\text{Li}1.01\text{Mn}2\text{O}_4$	2.5	0.80
実施例1-2	$\text{Li}1.02\text{Mn}1.98\text{Co}0.02\text{O}_4$	1.6	0.52
実施例1-3	$\text{Li}0.96\text{Mn}1.90\text{V}0.10\text{O}_4$	4.0	1.36
実施例1-4	$\text{Li}1.0\text{Mn}1.8\text{Ni}0.2\text{O}_4$	3.1	1.45
実施例1-5	$\text{Li}1.00\text{Mn}1.85\text{Fe}0.15\text{O}_4$	8.2	1.95
実施例1-6	$\text{Li}1.10\text{Mn}1.75\text{Cr}0.25\text{O}_4$	3.6	0.84
比較例1-1	$\text{Li}1.03\text{Mn}0.96\text{Ni}0.04\text{O}_4$	0.8	2.24
比較例1-2	$\text{Li}0.99\text{Mn}0.70\text{Al}0.30\text{O}_4$	2.3	3.58
比較例1-3	$\text{Li}1.08\text{Mn}1.85\text{Co}0.15\text{O}_4$	5.5	0.17

[0042] The telescopic cell was produced by the technique described below, having used the above-mentioned positive active material as the positive-electrode material, and the cell property was evaluated.

[0043] the positive-electrode production technique mixes graphite as an electric conduction agent 86% of the weight, and mixes 4 % of the weight (PVdF) of polyvinylidene fluorides as a binding agent 10% of the weight, and active material powder is distributed to an N-methyl-2-pyrrolidone (NMP) -- making -- a positive electrode -- a mixture -- it considered as the slurry This slurry was uniformly compressed into both sides of a band-like aluminum foil with a thickness of 20 micrometers after an application and xeransis and with the roller-press machine, and the band-like positive electrode was obtained. place  $2.8\text{g}/\text{cm}^3$  [ in addition, ] which measured the pack density of this positive electrode it was .

[0044] next, as a negative electrode, PVdF is mixed 10% of the weight to 90 % of the weight of powdered artificial graphites, and it distributes to NMP -- making -- a negative electrode -- a mixture -- it considered as the slurry this mixture -- the slurry was uniformly applied to both sides of copper foil with a thickness of 10 micrometers, and the band-like negative electrode was obtained by compressing with a roller-press machine after xeransis

[0045] The band-like positive electrode and band-like negative electrode which were produced as mentioned above were rolled about through the porous material polyolefine film many times, and the whorl type electrode field was produced. This electrode field was contained with the iron cell can which performed nickel plating, and the electric insulating plate has been arranged to vertical both sides of the concerned electrode field. Subsequently, the positive-electrode lead made from aluminum was drawn from collection \*\*\*\* of positive electrodes, and it welded to the pars basilaris ossis occipitalis of a cell can.

[0046] on the other hand -- the electrolytic solution -- the volume of ethylene carbonate and methylethyl carbonate -- the mixed solution whose mixing ratio is 1:1 --  $1\text{mol}/\text{dm}^3$  it becomes concentration -- as --  $\text{LiPF}_6$  It melted and nonaqueous electrolyte was prepared.

[0047] After pouring in the electrolytic solution finally into the cell can with which the above-mentioned electrode field was incorporated, by closing a cell can through an insulating obturation gasket, the relief valve, PTC element, and the cell lid were fixed, and the outer



diameter produced the cylinder system cell whose height is 65mm by 18mm.

[0048] The capacity factor after 200 cycles to initial capacity was again asked for the electric discharge capacity factor of 750mA of the discharge currents, and 4500mA of the discharge currents as a high-rate-discharge property as an index of the manganese elution from a positive electrode. A result is shown in Table 2.

[0049]

[Table 2]

	200サイクル後容量比 (%)	3C/0.5C高率放電容量比(%)
実施例1-1	88	72
実施例1-2	82	73
実施例1-3	91	78
実施例1-4	86	74
実施例1-5	83	71
実施例1-6	81	73
比較例1-1	71	74
比較例1-2	65	82
比較例1-3	85	38

	200サイクル後容量比 (%)	3C/0.5C高率放電容量比(%)
実施例1-1	88	72
実施例1-2	82	73
実施例1-3	91	78
実施例1-4	86	74
実施例1-5	83	71
実施例1-6	81	73
比較例1-1	71	74
比較例1-2	65	82
比較例1-3	85	38

	200サイクル後容量比 (%)	3C/0.5C高率放電容量比(%)
実施例1-1	88	72
実施例1-2	82	73
実施例1-3	91	78
実施例1-4	86	74
実施例1-5	83	71
実施例1-6	81	73
比較例1-1	71	74
比較例1-2	65	82
比較例1-3	85	38

[0050] If trituration mixture, pressurization molding, and baking are performed like an example 1-1 to 1-6, primary particle diameter and specific surface area are made to become within the limits of this invention, as shown in Table 2, only trituration mixture and baking are performed and one of primary particle diameter and the specific surface area has separated from the domain of this invention as the example of a comparison showed although the cycle capacity factor and high-rate-discharge capacity factor of a cell show a good value, a cycle capacity factor or a high-rate-discharge capacity factor will fall.

[0051] The experiment 2L raw material, Mn raw material, and nickel raw material were \*\*\*\*ed so that it might become a total of 2kg by composition of  $\text{Li1.0Mn1.8nickel0.2O}_4$ , and it mixed with the rotating type ball mill for 5 hours. It is the mixed raw material by the pressurization tablet molding machine 400kgf/cm<sup>2</sup> After having cast by the pressure and performing baking at various temperature in the atmospheric-air ambient atmosphere after that for 15 hours, the oscillatory-type ball mill performed trituration for 10 minutes. The obtained active material performed organization inspection and specific-surface-area measurement by the BET adsorption method, and calculated the value of primary particle diameter and specific surface area.

[0052] The value is shown in Table 3.

[0053]

[Table 3]

	烧成温度(°C)	1次粒子径(μm)	比表面積(m <sup>2</sup> /g)
实施例2-1	600	0.2	1.88
实施例2-2	780	3.5	1.34
实施例2-3	800	3.1	1.45
实施例2-4	900	8.2	0.39
比较例2-1	560	0.04	2.47
比较例2-2	920	13.8	0.18

[Table 3]

	烧成温度(°C)	1次粒子径(μm)	比表面積(m <sup>2</sup> /g)
实施例2-1	600	0.2	1.88
实施例2-2	780	3.5	1.34
实施例2-3	800	3.1	1.45
实施例2-4	900	8.2	0.39
比较例2-1	560	0.04	2.47
比较例2-2	920	13.8	0.18

[0054] The telescopic cell was produced by the same technique as an example 1, having used the above-mentioned positive active material as the positive-electrode material, and the cell property was evaluated. As an index of the manganese elution from a positive electrode, the capacity factor after 200 cycles to initial capacity was asked for the electric discharge capacity factor of 750mA of the discharge currents, and 4500mA of the discharge currents as a high-rate-discharge property. A result is shown in Table 4.

[0055]

[Table 4]

	200サイクル後容量比 (%)	3C/0.5C高率放電容量比(%)
実施例2-1	87	73
実施例2-2	84	75
実施例2-3	86	74
実施例2-4	83	72
比較例2-1	62	75
比較例2-2	88	32

[Table 4]

	200サイクル後容量比 (%)	3C/0.5C高率放電容量比(%)
実施例2-1	87	73
実施例2-2	84	75
実施例2-3	86	74
実施例2-4	83	72
比較例2-1	62	75
比較例2-2	88	32

[0056] That from which calcinates at the temperature of this invention within the limits, burning temperature separates from the domain of this invention like the example of a comparison although, as for that primary particle diameter and whose specific surface area are within the limits of this invention, the after [ a cycle of ] capacity factor and the high-rate-discharge capacity factor show the good value, and one of primary particle diameter and the specific surface area has separated from the domain of this invention like before understands that a cycle capacity factor or a high-rate-discharge capacity factor falls so that clearly from Table 4.

[0057]

[Effect of the invention] According to this invention, by specifying primary particle diameter and specific surface area of a spinel type lithium compound manganic acid ghost, there are few cell degradations by the manganese elution, and they can offer the positive active material for nonaqueous electrolyte cells which was excellent in the high-rate-discharge property, and a nonaqueous electrolyte cell so that clearly from the above explanation.

### Claims:

We claim,

[Claim]

[Claim 1] The positive active material for nonaqueous electrolyte cells characterized by the specific surface area which it comes to contain the lithium compound manganic acid ghost with a Spinel structure, and the size of the primary particle diameter forms the floc by 0.05 micrometers or more and 10 micrometers or less, and is measured by the BET adsorption method being a domain below 2m<sup>2</sup>/g more than 0.2m<sup>2</sup>/g.

[Claim 2] The above-mentioned lithium compound manganese active material is a positive active material for nonaqueous electrolyte cells of the claim 1 publication characterized by what is expressed with general formula  $LixMn_{2-y}MyO_4$  (however, it is  $0.90 \leq x \leq 1.4$  and  $y \leq 0.30$ , and M expresses any one or more kinds of the group which consist of Ti, V, Cr, Fe, Co, nickel, and aluminum.).

[Claim 3] The manufacture technique of the positive active material for nonaqueous electrolyte cells which mixes the start raw material of a lithium compound manganic acid ghost by predetermined composition, and is characterized by calcinating at the temperature of 600 degrees C or more and 900 degrees C or less after carrying out pressurization molding.

[Claim 4] The nonaqueous electrolyte rechargeable battery to which specific surface area which it has a Spinel structure, and the size of primary particle diameter forms the floc by 0.05 micrometers or more and 10 micrometers or less, and is measured by the BET adsorption method is characterized by using the lithium compound manganic acid ghost which is a domain below 2m<sup>2</sup>/g as a positive active material more than 0.2m<sup>2</sup>/g.

### **Abstract**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To make cycle characteristics compatible with high load characteristics.

**SOLUTION:** A positive electrode material for a nonaqueous electrolyte battery containing a lithium composite manganese oxide having spinel structure and a nonaqueous electrolyte using this active material are developed. The lithium composite manganese oxide having spinel structure has a primary particle size of 0.05  $\mu\text{m}$  or more but 10  $\mu\text{m}$  or less and forms coagulated particles, and has a BET specific surface area of 0.2  $\text{m}^2/\text{g}$  or less.